

Sensitive molecular determination of polycyclic aromatic hydrocarbons based on thiolated Calix[4]arene and CdSe quantum dots (QDs)

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Abstract A novel and sensitive electrochemical sensor based on the cone conformation of the supramolecule 25, 27-(3-thiopropoxy)-*p*-*tert*-butyl calix[4]arene has been developed for quantitative determination of polycyclic aromatic hydrocarbons (PAHs). The method works effectively by immobilizing calix[4]arenes on Fe₃O₄ magnetic nanoparticles. CdSe quantum dots were used as electrochemical labels. CdSe quantum dots (QDs) modified PAHs in competition with the sample PAHs were intercalated into calix[4]arenes supramolecules via a host–guest interaction through individual bowl-shaped calix[4]arenes. The stripping analysis of the cadmium dissolved from CdSe nanoparticles provided a sensitive method for the detection of PAHs in the samples. The signal decrease of the QDs was proportional to the increase in

the concentration of the PAHs. Under optimal conditions, among the five PAHs, the square wave voltammetry (SWV) response of QDs decreased linearly for anthracene and naphthalene in the range of 2.1×10^{-7} – 1.4×10^{-5} and 1.5×10^{-6} – 2.5×10^{-5} M, respectively. The calculated detection limits (3σ) were 20.1 ng mL^{-1} for anthracene and 105.5 ng mL^{-1} for naphthalene.

Keywords Cone 25 · 27-(3-thiopropoxy)-*p*-*tert*-butyl Calix[4]arene · Polycyclic aromatic hydrocarbons (PAHs) · CdSe QDs · Square wave voltammetry (SWV)

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) consisting of aromatic rings are classified as major organic contaminants in industrial and urban regions. They enter the environment from a variety of sources, including incomplete combustion of coal, oil, gas, and other organic substances such as tobacco [1].

Some PAHs have carcinogenic and mutagenic potential; hence, they are included in the U.S. Environmental Protection Agency's list of pollutants. However, many of these organic contaminants remain overlooked in programs designed to monitor environmental pollutants [2]. PAHs have low solubility in water, so treatments often require a complex extraction process, including preconcentration and separation procedures for sensitive detection of PAHs, which makes it a time-consuming and expensive task.

Examples of separation and detection techniques for PAHs include HPLC with fluorescence or absorbance detection [3, 4] or GC in combination with mass spectroscopy [5]. Such methods are sensitive and accurate, but they need fully equipped laboratories and skilled experts.

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So there is a demand for a cost effective and fast method to carry out sensitive and simple analysis of real environmental samples without complicated treatments.

In recent years, nanostructured materials have been extensively applied for the detection of PAHs and other pollutants [6, 7]. Calixarenes are a class of synthetic cyclo-oligomers formed via the phenol–formaldehyde condensation. Their inviting bowl-like shape can recognize other molecules and facilitate effective host–guest interactions and are capable of encapsulating a variety of aliphatic, aromatic, and ionic guest molecules [8, 9]. Their aromatic core is responsible for the molecular recognition behavior of calixarenes. It has a high affinity toward guest molecules through the involvement of either cation– π interactions, π – π stacking, or hydrophobic effects. These interactions are also active in aqueous media. Leyton et al. [10] used calix[4]arene molecules functionalized with Ag nanoparticles for surface-enhanced Raman spectroscopy to detect trace PAHs. Interactions between calixarenes and numerous macromolecules have been used in ion-selective membrane electrodes [11–13], electrophoresis [14–16], and chromatography [17, 18].

With the development of nanoscience and nanotechnology, various nanoparticles and quantum dots (QDs) have been widely used for labeling [19–23]. QDs are often used to enhance sensitivity in electrochemical stripping based analyses for the detection of trace biomolecules, because of their characteristics such as nanometer size and modifiable surface [24].

This work reports a simple and sensitive method to monitor PAHs using a competitive complex formation assay between QD/PAHs and target PAHs over thiolated calix[4]arene supramolecules.

2 Materials and methods

2.1 Reagents

Cadmium oxide (CdO, 99.99 %), selenium powder (Se, 99.99 %), Oleic Acid (technical grade), trioctylphosphine, and Octadecene (ODE, 90 %) were purchased from Sigma-Aldrich. 3-mercaptopropionic acid (MPA, 99 %); toluene, butanol, acetone, dimethylformamide (DMF), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, >99 %), ammonium hydrosulfide, ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, >99 %), ammonium hydroxide (25 wt%), and potassium carbonate were obtained from Fluka. All PAH standards were of 98–99 % purity and were dissolved in water and ethanol or acetonitrile in the ratio of 2:1. All PAH samples including naphthalene (Na), anthracene (A), benzo[a]anthracene (BaA), phenanthrene (Phe), fluorene (Fl), and chrysene (Chr) were purchased from Sigma-Aldrich.

2.2 Apparatus

All electrochemical measurements were performed on a polarograph (Metrohm 757) using a three-electrode system consisting of an Ag/AgCl reference electrode, a platinum auxiliary electrode, and a hanging mercury drop electrode (HMDE) as the working electrode. Transmission electron microscope (TEM) images were obtained with a Zeiss EM 900, operating at 100 kV. The average particle size and size distribution were measured by Zetasizer Nano ZS90, Malvern Instruments Corp. UK in disposable polystyrene cuvettes. A Biochrom WPA Biowave II spectrophotometer was used for complex formation studies.

2.3 Synthesis of thiolated calix[4]arene

p-*tert*-Butyl calix[4]arene was prepared following Gustches' "one-pot synthesis" method [25]. Cone 25, 27-(3-bromopropoxy)-*p*-*tert*-butyl calix[4]arene was prepared by the reaction of *p*-*tert*-butyl calix[4]arene with 1,3-dibromopropane in the presence of K_2CO_3 [26]. The reaction of NH_4SH with Cone 25, 27-(3-bromopropoxy)-*p*-*tert*-butyl calix[4]arene in DMF gave ligand Cone 25, 27-(3-thiopropoxy)-*p*-*tert*-butyl calix[4]arene.

To a solution of NH_4SH (1 mmol, 0.051 g) in 20 mL DMF, (0.4 mmol, 0.36 g) of Cone 25, 27-(3-bromopropoxy)-*p*-*tert*-butyl calix[4]arene was added, and the mixture was stirred at room temperature for 8 h after which it was poured into distilled water (100 mL). The precipitate was filtered, and the residue was purified by thin-layer chromatography using *n*-Hexane/Ethyl acetate as eluent. Cone 25, 27-(3-thiopropoxy)-*p*-*tert*-butyl calix[4]arene was obtained in 45 % yield as a white powder.

2.4 Preparation of Fe_3O_4 /calix[4]arene nanoparticles

Fe_3O_4 nanoparticles were prepared according to a reported procedure [27], whereby 2.7 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 50 mL deionized water in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ mole ratio of 1:2. Ammonia (25 %) was then added to the solution at 80 °C under the condition of vigorous stirring until the pH reached 9.0–9.5. The solution was stirred for a further 30 min at room temperature, and the precipitate obtained was separated with a magnet and washed with water. The precipitate was redispersed in 20 mL of water, then additional 1 g sodium oleate was added and the solution was stirred at room temperature for 2 h. The solution was then concentrated to produce a black suspension. The deposit was separated by a magnet and then rinsed with water until the fluid became neutral. 100 mg of this Fe_3O_4 nanoparticle was mixed with 10^{-5} M of thiolated calix[4]arene, and the mixture was sonicated

for 24 h at room temperature to form the $\text{Fe}_3\text{O}_4/\text{calix}[4]\text{-arene}$ nanoparticle.

2.5 Preparation of modified CdSe QD/PAHs

CdSe nanocrystals were synthesized from CdO and elemental Se using a kinetic growth method in which the resulting particle size is dependent on the reaction time [28, 29]. The selenium precursor solution was prepared by heating a mixture of 30 mg Se and 5 mL 1-octadecene (tech., 90 %) in a 10-mL round-bottom flask clamped over a stirrer hot plate and adding 0.4 mL trioctylphosphine into it and stirring the solution with a magnetic stirbar. The Cd precursor was prepared by adding 13 mg CdO to a 25-mL round-bottom flask clamped in a heating mantle. To the same flask, 0.6 mL oleic acid and 10 mL octadecene were added. A thermometer capable of measuring 225 °C was inserted, and the flask was then heated to that temperature. When the temperature reached 225 °C, 1 mL of the selenium solution was quickly injected into the cadmium solution. The temperature was kept constant at 225 °C until the growth of the QDs was completed. To alter the solubility of the QDs, excess MPA with KOH solution was added to the same volume of QDs and stirred vigorously overnight. During the transfer of QDs to the aqueous phase, the toluene layer became colorless and did not fluoresce under UV.

All PAHs used for attachment with QDs were functionalized with amino groups. Attachment of QDs and amine capped PAHs was achieved via the formation of amide bonds. For this purpose, 1 mL of a 0.05 mM solution of the amino group capped PAHs was added to 1 mL of the

quantum dots solution. The labeling reaction was incubated at room temperature for 12 h with continuous stirring [30].

2.6 Electrochemical measurements

The dissolved Cd^{2+} solution was transferred into a 2 mL acetate buffer (pH 4.8) as a supporting electrolyte solution and measured with SWV using HMDE. The process of electrochemical stripping detection was performed with pretreatment at +0.5 V for 1 min, and scanning potential from -0.9 to -0.5 V (vs. Ag/AgCl). Anodic stripping voltammetry (ASV) parameters were as follows: deposition time of 180 s, equilibrium time of 30 s, amplitude of 25 mV, step potential of 5 mV, and frequency of 15 Hz.

3 Results and discussion

In this work, Fe_3O_4 functionalized thiolated calix[4]arene was used to perform a competitive assay to determine PAHs. In this assay, six PAHs including naphthalene, anthracene, benzo[a]anthracene, phenanthrene, fluorene, and chrysene were used as spiked target PAHs in competition with QD/PAHs nanostructures. The electrochemical signal of the sensor was generated from the detection of Cd^{2+} released from the QDs [30, 31].

3.1 Sensor fabrication process

The schematic illustration of the stepwise procedure for the fabrication of the sensor is shown in Fig. 1. The mixed

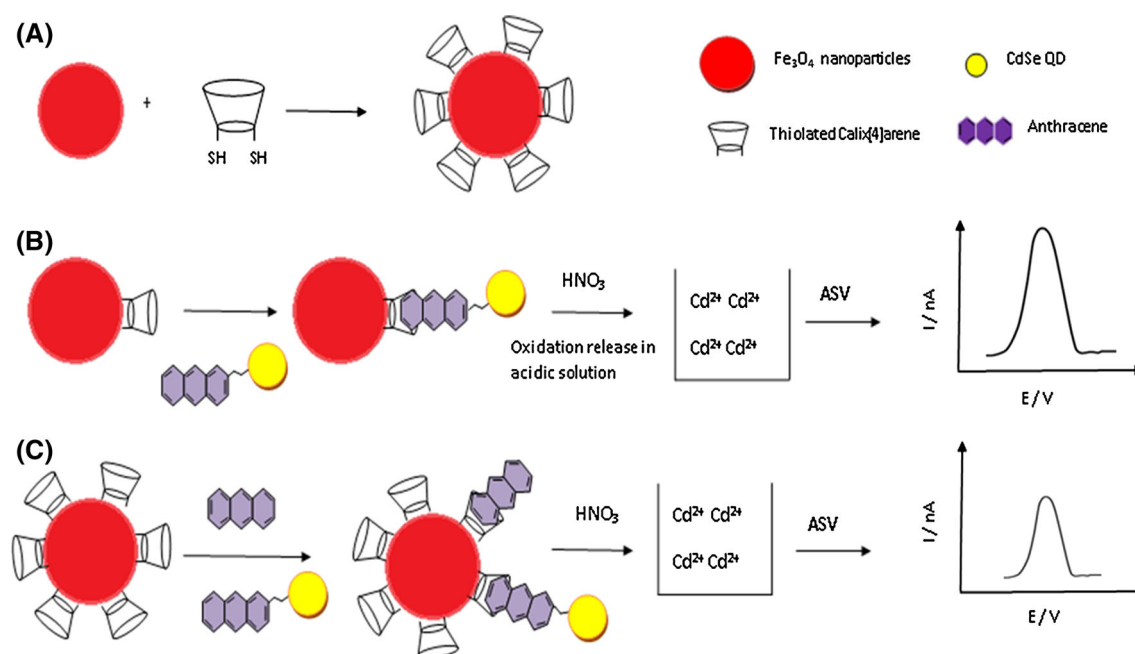
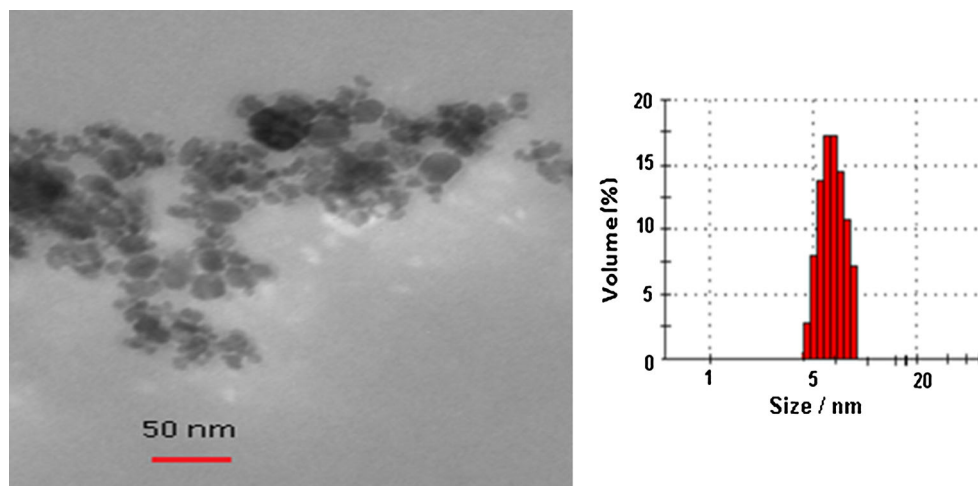


Fig. 1 The schematic illustration of the stepwise sensor fabrication and determination process

Fig. 2 TEM image of CdSe QD (*left*) and particle size histograms of CdSe QD (*right*)



solution was prepared by adding 2 mL of 1.1×10^{-6} M QD/PAHs to 1 mL of $\text{Fe}_3\text{O}_4/\text{calix}[4]\text{arene}$ (Fig. 1a). The mixed solution was stirred gently for 5 min and was then allowed to stand for a few minutes. After a magnetic separation, the residue was washed with water and resuspended in 0.2 M HNO_3 . The Cd^{2+} concentration of the solution was measured with the SWV method (Fig. 1b). In the next step, spiked solutions of PAHs and QD/PAHs were allowed to compete for calix[4]arenes over the Fe_3O_4 nanoparticles, and the Cd^{2+} concentration showed a significant decrease when measured again (Fig. 1c).

3.2 Characterization of the CdSe QD

Figure 2 shows the TEM image of CdSe QDs. The black and gray dots are both related to the CdSe QDs, with the black dots being formed by the overlapping of the gray dots. The TEM image shows that the QDs have uniform sizes, and the particle size histogram of CdSe QDs shows an average diameter of approximately 10 nm, which is similar to the results cited in other reports [22].

3.3 Formation of $\text{Fe}_3\text{O}_4/\text{calix}[4]\text{arene}$ complex

The attachment of thiolated calix[4]arenes to Fe_3O_4 magnetic particles was investigated through sensor fabrication. First, the UV–Vis spectra of thiolated calix[4]arenes in chloroform was obtained (Fig. 3a). Then, the attachment of thiolated calix[4]arenes to Fe_3O_4 magnetic particles was carried out by following the previous steps. Figure 3b displays the absorbance spectra of the residual solution after the magnetic separation of $\text{Fe}_3\text{O}_4/\text{calix}[4]\text{arene}$ complex, which shows a remarkable decrease in intensity. This decrease in calix[4]arene concentration is due to the formation of $\text{Fe}_3\text{O}_4/\text{calix}[4]\text{arene}$ complex and the removal of calix[4]arenes from the solution. Thus, this finding strongly

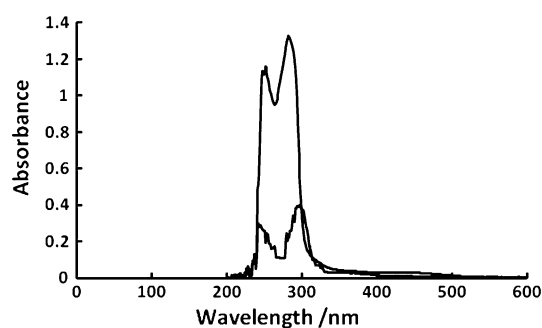


Fig. 3 Absorption spectra of *a* calix[4]arene in chloroform (10^{-5} M) *b* residual solution after the magnetic separation of $\text{Fe}_3\text{O}_4/\text{calix}[4]\text{arene}$ complex

approves our hypothesis regarding the formation of the complex.

3.4 Optimization of electrochemical detection conditions

To improve the sensitivity for PAH quantification, the concentration of QD-modified PAHs was optimized. The effect of the QD-modified anthracene on the electrochemical response of the fabricated sensor is shown in Fig. 4. It is obvious that the SWV peak current increased upon increasing the anthracene concentration and leveled off at ca. $0.2 \mu\text{g mL}^{-1}$. Thus, at this concentration of QD/anthracene, the maximum capacity of the calix[4]arene holes available on the Fe_3O_4 magnetic particles are occupied. Hence, beyond this concentration, there is no distinct change in the electrochemical response of the sensor.

The effect of pH on the ASV response of Cd^{2+} was investigated in the range of 3–6 [30]. As shown in Fig. 5, the current response reached its maximum at pH 4.8. This

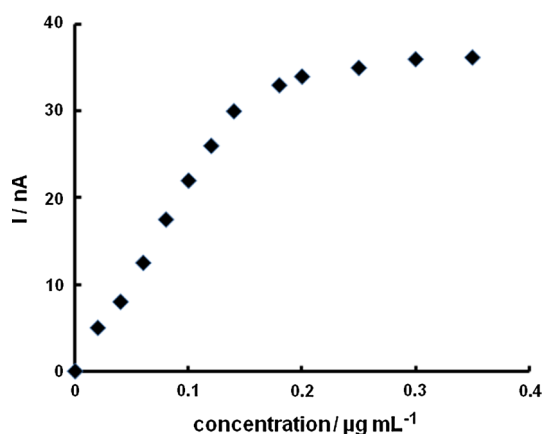


Fig. 4 Dose response of 0.02–0.4 $\mu\text{g mL}^{-1}$ QD-modified anthracene on the electrochemical response

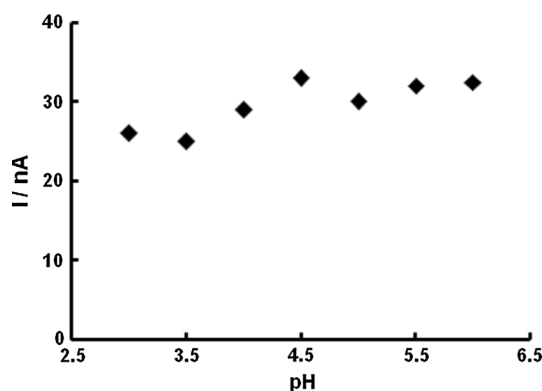


Fig. 5 Effect of pH on the ASV response of Cd^{2+}

pH level was chosen as the optimum condition for all ASV determinations.

3.5 Diagnostic performance of the sensor

Under these optimal conditions, the proposed method was used to detect PAHs based on thiolated calix[4]arene. The detection of the target PAH was monitored by means of square wave voltammetric response of QDs attached to calix[4]arene sites in the absence and presence of target PAH. The comparative SWV response of the nanostructures in the absence and presence of 0.5 $\mu\text{g mL}^{-1}$ target anthracene is shown in Fig. 6. As can be seen in Fig. 6, there is a significant decrease between the signals produced for the determination of Cd^{2+} ions at -0.72 V . As expected, in the presence of anthracene spiked solution as the target PAH, the peak current decreased to about half as compared to that in the absence of spiked anthracene. This decrease may be attributed to the massive accumulation of

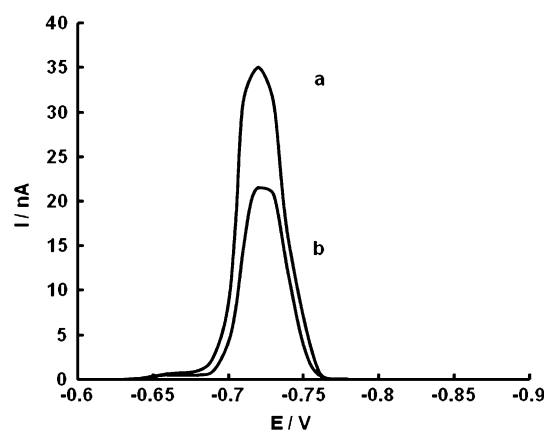


Fig. 6 SWV detection of Cd^{2+} *a* in the absence and *b* presence of 0.5 $\mu\text{g mL}^{-1}$ target anthracene. Amplitude of 25 mV, step potential of 5 mV, and a frequency of 15 Hz

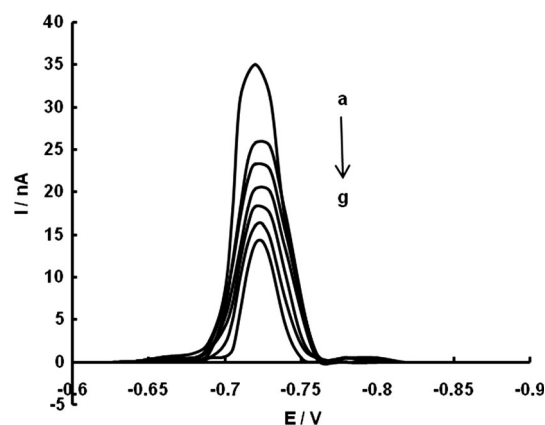


Fig. 7 SWV detection of Cd^{2+} *a* in the absence and *b* presence of 0.3 $\mu\text{g mL}^{-1}$, *c* 0.5 $\mu\text{g mL}^{-1}$, *d* 1.0 $\mu\text{g mL}^{-1}$, *e* 1.5 $\mu\text{g mL}^{-1}$, *f* 2.0 $\mu\text{g mL}^{-1}$, and *g* 2.5 $\mu\text{g mL}^{-1}$ target anthracene

target anthracene instead of anthracene/QD complex in the calix[4]arene holes over the magnetic nanoparticles.

Previous reports have demonstrated that the inclusion-type interaction of calixarenes with PAHs is because of its high affinity for guest molecules through the involvement of π – π stacking effects [32]. The upper ring diameter of calix[4]arenes is reported to be about 4.9 Å, so it matches more efficiently with the diameter of anthracene 5 Å [10], a fact which also confirms the results of this experiment.

Figure 7 shows the SWV response of the sensor to the different concentrations of anthracene. The peak current, attributed to Cd^{2+} , decreased with increasing concentration of anthracene. The difference of electrochemical signal of the QD-modified anthracene in the absence and presence of target anthracene (ΔI) increased with the increase in the anthracene concentration and leveled off at ca. 3 $\mu\text{g mL}^{-1}$ (Fig. 8). As can be seen, the dose–response curve for the

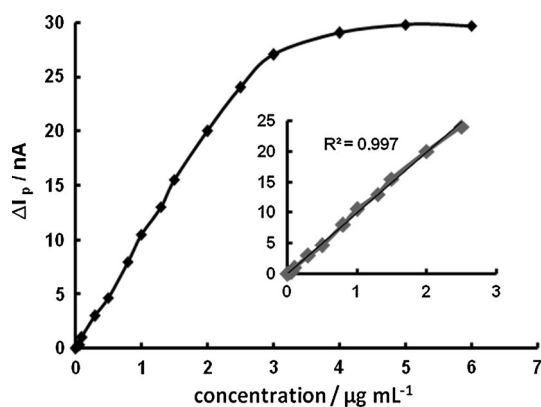


Fig. 8 Plot of ΔI (difference between the SWV signal of Cd^{2+} in the presence and absence of target anthracene) versus target concentration. *Inset* related to the calibration curve at the concentration range of up to $2.5 \mu\text{g mL}^{-1}$

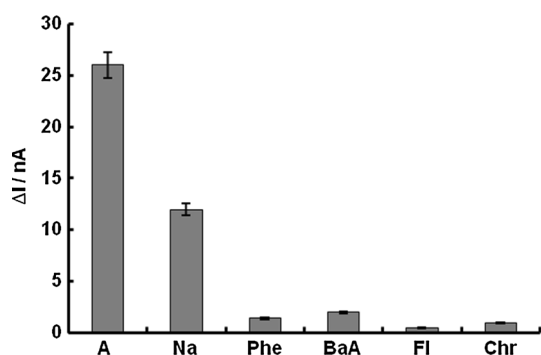


Fig. 9 The electrochemical response of the assay in different PAH solutions including *A* Anthracene, *Na* Naphthalene, *Phe* Phenanthrene, *BaA* Benz(a)anthracene, *Fl* fluorene, and *Chr* chrysene. The concentration of all PAHs was kept at $2 \mu\text{g mL}^{-1}$

target anthracene showed a linear range from 0.3 to $2.5 \mu\text{g mL}^{-1}$ with a correlation coefficient of 0.997 (*inset* of Fig. 8).

Under the optimal conditions, the SWV response of the QDs decreased linearly with increasing naphthalene concentration within the range of 1.5×10^{-6} – 2.5×10^{-5} M. The detection limits (3δ) were calculated and determined as 20.1 ng mL^{-1} for anthracene and 105.5 ng mL^{-1} for naphthalene. The reproducibility of the sensor was also tested. The relative standard deviations established at three replicate measurements with anthracene and naphthalene samples were 5.3 and 8.7 %, respectively. Unlike some of the related chromatographic or spectroscopic techniques reported [33–35], which are complicated in terms of practical application, this method facilitates the determination of PAHs by means of a sensitive SWV signal.

Table 1 Recovery studies of anthracene in tap water samples ($n = 3$)

Sample	Standard concentration of anthracene (μM)	Determined by sensor (μM)	Recovery (%)	RSD (%)
1	0.5	0.46	92	4.8
2	1.0	1.13	113	6.2
3	10	10.92	109.2	3.4

The selectivity of the assay was examined in the presence of different PAHs including anthracene, naphthalene, benzo[a]anthracene, phenanthrene, fluorene, and chrysene. As can be seen in Fig. 9, the prepared sensor shows no significant selectivity toward phenanthrene, fluorene, chrysene, and benzo[a]anthracene.

3.6 Application on real samples

A preliminary evaluation of the recovery of the proposed sensor on tap water samples was performed. For the recovery test, tap water samples were spiked with different known anthracene concentrations and were accordingly analyzed. The results are summarized in Table 1. As can be seen, the results are in good agreement with the given concentration, with the average recoveries ranging from 92 to 113 % ($n = 3$). These results indicate that this method is highly accurate and precise. Thus, it can be used as an alternative for anthracene determination in water samples.

4 Conclusions

This work demonstrates a novel electrochemical recognition method for PAHs in aqueous solution using thiolated calix[4]arenes and QDs as label. As a result of remarkable changes in the electrochemical signal of QDs for different PAHs based on the cavity size of calix[4]arene, this sensor provides a selective assay for PAHs. Under the optimal conditions, the relative electrochemical signals of Cd^{2+} decreased with increase in the concentrations of anthracene and naphthalene in the range of 2.1×10^{-7} – 1.4×10^{-5} and 1.5×10^{-6} – 2.5×10^{-5} M, with the corresponding detection limits (3δ) of 20.1 ng mL^{-1} and 105.5 ng mL^{-1} , respectively. Due to the important and critical properties of the proposed sensor such as simplicity, selectivity, and low cost, future studies may be extended to include the sensitive detection of different PAHs in different environmental samples using different calix[4]arenes and QD labels.

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